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Title: *Novel Energy Sources -Material Architecture and Charge Transport in Solid State Ionic Materials for Rechargeable Li ion Batteries*

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Program Scope

Since its introduction in the consumer market at the beginning of 1990s by Sony Corporation 'Li-ion rechargeable battery' and '*LiCoO₂ cathode*' is an inseparable couple for highly reliable practical applications. However, a separation is inevitable as Li-ion rechargeable battery industry demand more and more from this well serving cathode. Spinel-type lithium manganate (*e.g.*, *LiMn₂O₄*), lithium-based layered oxide materials (*e.g.*, *LiNiO₂*) and lithium-based olivine-type compounds (*e.g.*, *LiFePO₄*) are nowadays being extensively studied for application as alternate cathode materials in Li-ion rechargeable batteries.¹⁻⁷

Primary goal of this project was the advancement of Li-ion rechargeable battery to meet the future demands of the energy sector. Major part of the research emphasized on the investigation of electrodes and solid electrolyte materials for improving the charge transport properties in Li-ion rechargeable batteries. Theoretical computational methods were used to select electrodes and electrolyte material with enhanced structural and physical properties. The effect of nano-particles on enhancing the battery performance was also examined. Satisfactory progress has been made in the bulk form and our efforts on realizing micro-battery based on thin films is close to give dividend and work is progressing well in this direction.

Recent Progress

In some cathode materials *e.g.* *LiMn_{2-x}N_xO₄* (*x*= Ni, Nd, Cr, Rh), we have optimized the process parameters to improve structural stability and electrochemical properties. We have successfully synthesized nanostructured Carbon-LiFePO₄ composite cathode materials with conventional solid-state route to address the electronic conductivity and Li-diffusion. Further steps are still going towards finding the new cathode materials for high energy density Li ion rechargeable batteries. We have investigated ion transport and electrochemical behavior of some polyethylene oxide (PEO) based nano-composite solid polymer electrolytes. In relation to Li ion rechargeable batteries, the recent results of our group are describe below

First-principles computations

First-principles computations are considered to be an important theoretical tool to predict the properties of materials. Computational modeling has been used to investigate rechargeable battery materials and prescreen their compositions when designing new cathode materials for battery applications. In an attempt to design and prescreen new cathode materials, we have computed the average intercalation voltages, lattice parameters, and density of states of a number of promising spinel cathode materials by inserting lithium ions into 2nd-row transition-metal oxides. These type cathode materials have the problem of capacity fading and limited cycleability in the 4V as well as 3V regions.

Table 1. $\text{Li}_2\text{Ni}_x\text{Mn}_{16-x}\text{O}_{32}$ and $\text{Li}_0\text{Ni}_x\text{Mn}_{16-x}\text{O}_{32}$ free and Li partial intercalation energies (eV). Li ultra soft pseudopotential energy of 0.238eV is removed.

Number of Ni atoms	E(free) Li_2	E(free) Li_0	E(int) (eV)
0	-415.24930	-406.13046	-4.31
1	-409.77669	-400.21038	-4.54
4	-394.068831	-384.000798	-4.80

In Table 1 we present the free energies of the $\text{Li}_x\text{Mn}_{16}\text{O}_{32}$ system, obtained after the full optimization of the cell. E(int) is the intercalation energy for one Li atom and is approximately equal to the cell voltage. Theoretical curve of partial Li intercalation is nearly constant with somewhat lower value for single Li intercalation. The further increase of the number of Li atoms (larger than 8) significantly lowers theoretical cell voltage to the values smaller than 3.5 volts, which is observed experimentally.

To further explain the improvement in the capacity, we have performed a set of DFT calculations to identify the minimum-energy Li^+ diffusion path in the cathode. In the optimized cell containing two Li atoms, a single Li atom was moved from one site to the next site. In figure 14, we present the minimum-energy Li^+ hopping path in the spinel $\text{Mn}_{15}\text{Ni}_1\text{O}_{32}$ super-cell, a super-cell with one Ni ion substitution. The minimum-energy pathway was computed to determine the activation energy required for the hopping to occur. The dark sphere represents the point in the path with the largest activation energy for hopping. The oxygen atoms strongly coordinate to the Li atoms and lattice becomes somewhat distorted. The same procedure was repeated for the super-cells with more Mn replacements with the Ni. Up to four Mn were replaced with the Ni near the Li pathway in order to maximize the effect of the substitution on the mobility of Li ion. In reality, the experiment has no means to produce cathodes with Ni replacements of the specific sites. The statistical average of all possible replacements would be more realistic. However, we found that the results are not very sensitive to the number of the replacements, but they depend on specific order of replacements. The results imply significant improvement in Li ion mobility. The significant reduction – by as much as 32 percent - in activation energy was observed initially with a single Mn replacement by Ni atom in the site nearest the hopping path (See figure 1).

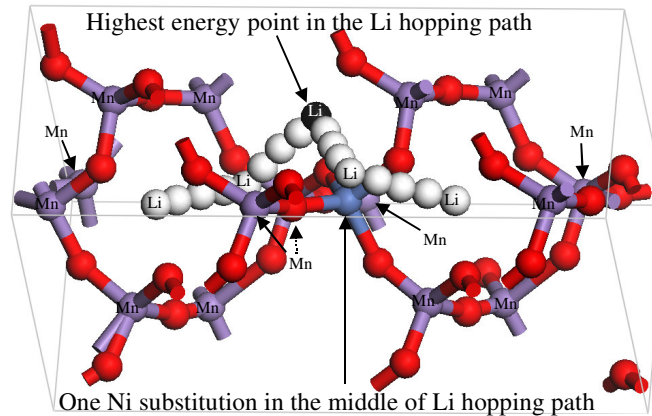


Figure 1. Estimated Li^+ hopping path in the $\text{Mn}_{15}\text{Ni}_1\text{O}_{32}$ super-cell.

This Ni site has the shortest distance to the Li pathway, having the greatest effect on the Li ion mobility. The super-cell structure with four Ni substitutions at sites further

away from the Li ion path gives rise to a slightly lower effect - a 27 percent reduction in activation energy. The Mn replacements by four Ni at structurally equivalent positions are more realistic as this arrangement minimizes the free energy, and hence experimentally achievable. The extrapolation of the result in $\text{Li}_2\text{Mn}_{12}\text{Ni}_4\text{O}_{32}$ supports our experimental results on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. Statistically estimated average activation energy was in the range of 2100meV and hence, a 13 percent improvement over pure Mn_2O_4 spinel cathode. In figure 2, we plotted density of states against the one-electronic energy, relative to the Fermi level. As was expected the pure Mn_2O_4 spinel structure feature sharp peaks in the density of states plot. This is explained by high symmetry of the lattice. Substitutions of Mn by Ni significantly reduce the symmetry, and density of states plot has more continuous form.

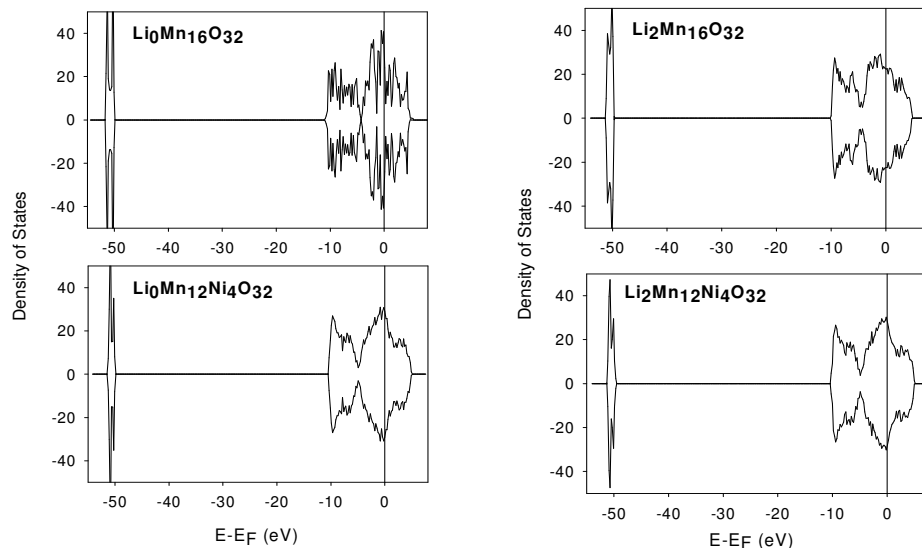


Fig.2 Comparison of the operating voltage plateaus of $\text{LiMn}_2\text{O}_4/\text{LiPF}_6+(\text{EC}+\text{DMC})/\text{Li}$ and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4/\text{LiPF}_6+(\text{EC}+\text{DMC})/\text{Li}$ coin cells. With 0.5 Ni substitutions in the octahedral Mn site, a clear shift in 4.1V plateau to 4.7V was observed.

Cathode materials

Spinel cathode materials e.g $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$, $\text{LiMn}_{1.99}\text{Ce}_{0.01}\text{O}_4$, and $\text{LiMn}_{1.5}\text{Ni}_{0.46}\text{Rh}_{0.04}\text{O}_4$ have been synthesized by sol-gel process. The structural and electrochemical properties of these cathodes were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy. Cyclic voltammetry, and charge-discharge studies on coin cells were tested for many charge-discharge cycles. The charge-discharge characteristics of the coin cell with $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes were performed in the 3.0–4.8 V range. An initial discharge capacity of $\sim 140\text{mAh g}^{-1}$ was obtained with 94% initial discharge capacity retention after 50 cycles. The charge-discharge characteristics for $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$ cathode materials were obtained in 3.4–4.3 V voltage range and the initial discharge capacity of this material were found to be about 149mAh g^{-1} . The results show that by doping with small concentration of rare-earth element Nd, the capacity fading is considerably reduced as compared to the pure LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes. Encouraged by this result we prepared $\text{LiMn}_{1.99}\text{Ce}_{0.01}\text{O}_4$ spinel material and the charge-discharge characteristics were obtained in 3.5 V – 4.8 V voltage range. The initial discharge capacities of $\text{LiMn}_{1.99}\text{Ce}_{0.01}\text{O}_4$ and was 134mAh/g . The coin cells were tested for up to 25 charge-discharge cycles and after 25 cycles the discharge capacities were only 79.5mAh/g suggestive of significant fading with Ce doping. Where as in the case of $\text{LiMn}_{1.5}\text{Ni}_{0.46}\text{Rh}_{0.04}\text{O}_4$, the initial discharge capacity was found to be about 154mAh/g and capacity retention was about 93.5% after 50 charge-discharge cycles. Hence, by doping with rare earth materials always won't improve the battery performance and

hence proper selection is of importance to improve the electrochemical properties of the batteries. Next we considered $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode material with ZnO coating. It was found that the ZnO coated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode materials showed improved discharge capacity ($\sim 146\text{mAh/g}$) as compared to the pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($\sim 140\text{mAh/g}$). The discharge capacity retention after 50 cycles was also improved to 97% compared to the 94% of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode materials.

We performed first principle calculations using VASP on the cation substitution of 4d transition metals (Mo and Rh) in $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{M}_{1/3}\text{O}_2$ cathode materials. The density of states for fully lithiated and delithiated $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Mo}_{1/3}\text{O}_2$ was found to be slightly positive (Fig **), indicating that the stoichiometric ratio of this material is unfavorable. On the other hand, the density of states for fully lithiated and delithiated $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Rh}_{1/3}\text{O}_2$ was found to be negative (Fig **), indicating the energetically favorable form of these phases. They also calculated the metal oxygen bond lengths and concluded that Mn remains in +4 state and only Ni and Rh participate in the electrochemical reaction.

We have synthesized $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$ bulk cathodes ($x = 0.0 - 1.0$) using a cost effective chemical solution route and studied its structural stability using XRD, XPS, and micro-Raman techniques. The first discharge capacity of $\sim 140\text{mAh/g}$ was obtained with a good cycleability (up to 50 cycles) in the voltage range of 3.0 – 4.2V. The effect of simultaneous cobalt as well as aluminum doping was studied to understand their effect on the phase formation behavior and electrochemical properties of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ for rechargeable batteries.

A simple solution route has been developed to prepare $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material. Synthesized $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ had a well-defined hexagonal layered structure with very low cation mixing. XPS analysis showed that the Ni^{+2} and Mn^{+4} ions are present in the prepared $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ material, and Mn remained as Mn^{+4} throughout the electrochemical cycling. It was also found that the $\text{Ni}^{+2}/\text{Ni}^{+3}$ and $\text{Ni}^{+3}/\text{Ni}^{+4}$ redox couples were involved during electrochemical (de) intercalation of Li^{+1} . In the voltage range 2.5–4.5 V the present $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ showed a moderately high initial discharge capacity (130mAh/g) and a good capacity retention (93.77%) after 30 cycles. Raman analysis showed the structural stability of the prepared $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ during electrochemical cycling.

The discharge capacities of $\text{LiNi}_{0.80}\text{Co}_{0.20}\text{O}_2$ and $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes, measured at constant current densities of 0.45mA cm^{-2} in the cut-off voltage range of 3.2–4.3 V, were 100 and 136mAh g^{-1} , respectively. We then concentrated on the preparation of layered $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Mn}_y)\text{O}_2$ and $\text{Li}(\text{Ni}_{1-x}\text{Mn}_x)\text{O}_2$ cathode materials. $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ cathode materials were synthesized by solid-state reaction route. Electrochemical studies showed single redox reaction and a maximum charging and discharging capacity capacity was found as 140mAh/g and 132mAh/g , respectively. The discharge capacity retention after 20 cycles was 86 %.

We have synthesized $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (LNCO) cathode material by solid-state route as a most attractive candidates for high power electronic devices. The discharge capacity and the capacity retention of LNCO cathode are found to be $\sim 100\text{mAhg}^{-1}$ and $\sim 63\%$, respectively. Molybdenum doping, replacing parts of cobalt ion in LNCO lattice increases the discharge capacity ($\sim 157\text{mAh g}^{-1}$) and improve its capacity retention characteristics. Through X-ray Rietveld analyses, we have found that Mo doping increases the inter-slab spacing between the (Co,Ni)O₂ octahedral layers which provides easier Li^{1+} intercalation leading to improved electrochemical properties in the modified cathode.

$\text{Li}[\text{Mn}_{0.5-x}\text{Cr}_{2x}\text{Ni}_{0.5-x}]\text{O}_2$ ($0 < 2x < 0.2$) ($\text{Mn/Ni} = 1$) cathode materials have been synthesized by a solution method. X-ray diffraction patterns of the as-prepared materials were fitted based on a hexagonal unit cell ($\alpha\text{-NaFeO}_2$ layer structure). The extent of Li/Ni intermixing decreased, and layering of the structure increased, with increasing Cr content. Electrochemical cycling of the oxides, at 30°C in the 3–4.3V range vs. Li/Li^+ , showed that the first charge capacity increased with increasing Cr content. However,

maximum discharge capacity ($\sim 143 \text{ mAhg}^{-1}$) was observed for $2x = 0.05$. X-ray absorption near edge spectroscopic (XANES) measurements on the K-edges of transition metals were carried out on pristine and delithiated oxides to elucidate the charge compensation mechanism during electrochemical charging. The XANES data revealed simultaneous oxidation of both Ni and Cr ions, whereas manganese remains as Mn^{4+} throughout, and does not participate in charge compensation during oxide delithiation.

We have prepared nanostructured Carbon- LiFePO_4 composite cathode materials with conventional solid-state route to address the electronic conductivity and Li-diffusion. The orthorhombic olivine structure without any impurity was obtained at 650°C . The average LiFePO_4 particle size was $\sim 80 \text{ nm}$ and were coated with residual carbon. The cyclic voltammograms showed only a pair of peaks corresponding to the anodic and cathodic reactions. The irreversible capacity loss in the first cycle was 5 mAh/gm , and the Coulombic efficiency was 97%. The first discharge capacity was 157 mAh/g , equivalent to 93% of the theoretical capacity ($\text{Fe}^{2+}/\text{Fe}^{3+}$ redox efficiency). Capacity retention after 80 cycles was $\sim 98\%$ and hence insignificant capacity fading.

Thin Film cathode materials

Nanocrystalline lithium manganate thin films ($\text{Li}_x\text{Mn}_2\text{O}_4$; $x = 1.0\text{--}1.4$) have been deposited on Pt-Si ($\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$) substrates using a cost-effective solution growth technique. By optimizing the deposition parameters and heat treatment schedule, we obtained dense, nano-size, and cubic spinel lithium manganate thin films with narrow grain size distribution. The nanocrystalline nature of the films was revealed by the SEM micrographs and the surface morphology studied using AFM. Finally, the electrochemical properties (cyclic voltammetry and constant current measurements) of these films were analyzed using a home made three-electrode cell and Gamry Battery tester instrumentation. These films exhibited excellent discharge capacity (close to the theoretical limit of LMO) in the cut of voltage range of $4.2\text{--}3.4\text{V}$ and discharge current densities ranging $30\text{--}180 \mu\text{Ah cm}^{-2}$. However, rapid capacity fading was observed within the first few charge-discharge cycles followed by a marginal capacity loss with additional charge-discharge cycles. The formation of the Jahn-Teller active Mn^{3+} during electrochemical cycling was completely ruled out from the XPS analysis. Also the very consistent value of $[\text{Mn}^{3+}/\text{Mn}^{4+}]$ ratio before and after electrochemical cycling on the surface of the film revealed good quality of the films. The formation of a prominent layer of fluoride species deposited over the cathode surface during the repeated cycling was revealed by XPS measurements. Finally, the formation of the fluoride layer was concluded as a passive layer that causes the initial capacity drop during first few cycles of the cell performance. At present we are extending this thin film cathode research on other selected material showing encouraging properties based on the bulk cathode studies, both on layer and olivine systems.

Nanostructured cathode materials

It is known that reduction in path lengths for electron and ion transport can provide materials with high-rate capabilities. The energy required for driving electrochemical phase transitions are minimized within nano-regime crystallites, materials, which are poorly conductive, could be electrochemically “wired” on the surface. Therefore, it is increasingly apparent that promising electrochemical characteristics can result from the creation of nanostructures, or nanostructure domains within electroactive materials.

We have successfully synthesized nano-crystalline (diameter $< 100 \text{ nm}$) lithium manganate (LMO) particles by an acetate based chemical solution route. In the $4.2\text{--}3.4\text{V}$ range at 0.98 C discharge rate, the capacity of nano-crystalline LMO was 120mAh/g . However, even in the 4V ranges, severe capacity fading was observed when these

cathodes were cycled at constant current of 0.98 C. By analyzing the low scanned X-ray diffractograms of as prepared and cycled composite cathodes, we found that both the lattice strain as well as crystallite size of LMO particles were increased after the charge–discharge cycling. The XPS analysis in conjunction with the micro-Raman spectroscopy indicated that at the surface of LMO particles, the Mn^{3+} ion contents were increased after charge–discharge cycling. The increase of Mn^{3+} ion contents as well as lattice strain could be related with the formation of tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ type compound at the surface of LMO particles having otherwise cubic spinel structure. The reason for the severe capacity fading of nano-crystalline LMO powders were believed to be due to the onset of the Jahn–Teller distortion towards the end of the discharge. By simultaneous Li and Al doping (replacing Mn in the octahedral 16d site), the average oxidation state of Mn ions in virgin LMO electrodes was increased and hereby the onset of cubic to tetragonal structural transition (Jahn–Teller) was delayed. Although the discharge capacity of these co-cation doped lithium manganate was reduced, but their cycleability was dramatically improved.

Electrolytes

Severe reactivity of lithium metal greatly limits the choice of usable electrolytes and incurs safety problems for the commercialization of rechargeable batteries. Because liquid electrolytes have a gradually degradable charge–discharge cycle performance partly due to reaction with electrode materials and volatile problems, solid or solid-like electrolytes are highly in demand for high-capacity Li batteries. Polymers like polyethylene oxide (PEO), polyphenylene oxide (PPO), polyvinyl pyrrolidone (PVPD), and polyacrylonitrile (PAN) with Li salt can be used for the synthesis polymeric electrolytes. However, it suffers from low ionic conductivity (ca. 10^{-7} – 10^{-5} S cm^{-1}) at room temperature^{8–11}. In order to overcome this problem, consistent research efforts have been made to improve the ionic conductivity in PEO–LiX ($\text{X}=\text{ClO}_4^-$, CF_3SO_3^- , BF_4^- , PF_6^- etc.) composite polymer electrolytes.

We have synthesized polymer electrolytes consisting of polyethylene oxide (PEO) and LiCF_3SO_3 by solution casting method as a function of EO/Li ratio. An increase in the glass transition temperature of the polymer electrolytes with increasing Li salt content suggested the coordination of the Li ions to the oxygen atoms of polymer backbone. Dielectric spectroscopic studies were performed to understand the ion transport process in polymer electrolytes. The maximum dc conductivity of 1.3×10^{-6} S/cm was obtained for EO/Li \approx 24. The conductivity decreased with further addition of salt, similar to the variation of T_g with EO/Li, suggesting the decrease in the conductivity was due to the ion-pairing at higher salt concentrations. The ac conductivity analysis revealed the existence of nearly constant loss (NCL) contribution at lower temperatures. The dielectric loss spectra showed the presence of one relaxation for all compositions, which is associated with the motions of the Li ion coordinated polymer segments. The temperature dependence of the relaxation times and the conductivity followed the Vogel–Tamman–Fulcher (VTF) equation yielding qualitatively similar pseudoactivation energies, which suggested strong coupling between the ionic conductivity and the segmental relaxation in the polymer electrolytes.

Addition of ceramic nanoparticles (e.g., TiO_2 , SiO_2 , etc.) into the polymer matrices has been reported to reduce T_g and increase the Li^+ transference number. Little systematic effort has so far been made to understand the underlying mechanism that leads to the improvement of Li ion conductivity at room temperature. We recently investigated ion transport and electrochemical behavior of some polyethylene oxide (PEO) based nano-composite solid polymer electrolytes, and our result clearly sheds some light on the mechanism of conductivity enhancement in nano-composite polymer electrolytes using dielectric spectroscopy. To summarize, we synthesized nano-fibrous polymer electrolytes, for the first time, with ambient conductivity of 2×10^{-5} S/cm.

The improved thermal and electrochemical stability of the electrolyte is attributed to the nano-morphological features. Based on our experimental results, we demonstrated that the nano-structured polymer electrolyte exhibits superior electrochemical, thermal stability and conducts better than the bulk. Although, we obtained an electrochemical window stability of up to 7 V, which is nearly 2.5 V higher than the reported value, the cyclability results conducted on all solid state batteries using this electrolytes indicated the need to further enhance the ambient conductivity to achieve good cyclability at room temperature.

Anode Materials

Carbon (including meso carbon micro beads, graphite powder, carbon nanotubes among other) materials, generally in the form powders with a polymeric binder, are typically used in lithium-ion battery electrodes. This binder reduces the effective area of the active material that is exposed to the electrolyte and often limits the temperature range over which the device can work due to the reduced thermal stability of available binders. Therefore, it is critical to develop electrode materials with substantially higher capacities than graphite. Binder-free direct depositions of nanostructured carbon films on Cu substrates are thus an attractive alternative to enhance the electrode's capacity and thermal stability. In the case of *anode*, our work thus addresses, *nanocomposite carbon, carbon nanotubes, titania and stannic oxide* in the nanocrystalline form with focus to electrode's capacity and thermal stability.

Nanocomposite carbon anode materials for rechargeable Li batteries were prepared by depositing nanocrystalline diamond, nanocomposite carbon and carbon nanotubes on a copper substrate. Films of bamboo-like carbon nanotubes (BCNTs) were grown directly on Cu substrates by hot filament chemical vapor deposition (HFCVD) without any catalysts. This is a new and efficient technique that yielded a large density of active sites. In the fabrication of coin cells, we use the above carbon-based materials as anodes and Li-metal as cathode. The electrochemical characterization of the carbon-based anodes is done by electrochemical techniques like cyclic voltammetry and charge-discharge measurements and are shown in Fig.3 for sulfur-doped nanocomposite carbon and BCNT thin film/(EC+DMC)/Li coin cell in 0-2 V range. CV results indicate the formation of a solid electrolyte interface. Sulphur doping in nanocomposite carbons is mainly to create defect sites in the graphite structure enabling lithium to intercalate into the defect sites. In the case of BCNT, the initial discharge capacity was found to be $880 \mu\text{Ahcm}^{-2}\mu\text{m}^{-1}$, which is greater than the volumetric theoretical capacity of graphite, i.e. $84 \mu\text{Ahcm}^{-2}\mu\text{m}^{-1}$. The reversible capacity remains at $205 \mu\text{Ahcm}^{-2}\mu\text{m}^{-1}$ after ten cycles. The nanocavities of the BCNTs appear to have a significant role in the large capacity for reversible Li insertion.

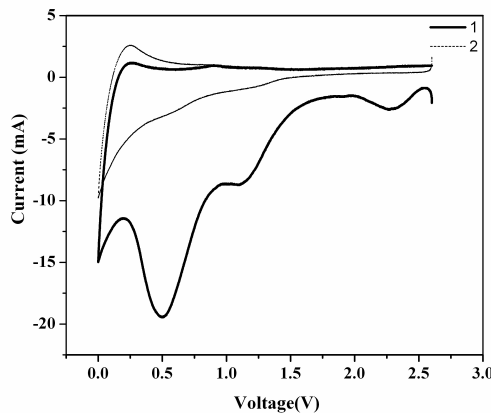


Fig.3 Cyclic voltammetry of BCNT thin film/(EC+DMC)/Li coin cell in 0-2 V range taken at a scan rate of 0.02 mV/s: (1) first cycle, (2) second cycle.

Bamboo-like carbon nanotubes (BCNTs) have been deposited by many researchers using different techniques like arc-discharge, laser vaporization, pyrolysis, chemical vapor deposition, microwave plasma enhanced chemical vapor deposition, and radio frequency magnetron sputtering. In most of the above deposition techniques, a metal catalyst was first solidified on the substrate in order to grow BCNTs. Among the few, multiwalled CNTs with bamboo-like cavity structure (BCNTs) also referred to as polymerized nano bell structure, have been investigated. The significance of our HFCVD technique is that it effectively reduces the prolonged steps involved in the conventional fabrication carbon nanotubes electrodes that involve deposition using metal catalysts, subsequent mixing with binders, and application to a metal surface. Unlike the common carbon nanotubes (CNTs) with an integral hollow cylindrical structure, the interior of BCNTs is divided by bent graphene sheets that form many separated cavities, analogous to the structure of bamboo trees. Hence, the exterior walls of the BCNTs have many edge planes that can support lithium insertion.

Apart from the carbon based anode materials we were concentrated in the development of titania and stannic oxide anodes. In present commercial lithium-ion batteries, graphite is a widely used anode material, but it has some disadvantages, such as electrical disconnection, structural deformation, and initial loss of capacity. The second class of materials includes tin, silicon, aluminum, and their oxides. Tin and tin oxide have received much attention. They can form various alloys with lithium and have different electrochemical capacities. These types of oxide anodes composed of oxides of tin are of considerable interest because, in principle, they can store over twice as much as lithium as graphite. During the first charging, tin oxide is reduced to tin, which is dispersed in matrix of lithium oxide. The metallic tin may then reversibly react with lithium to form a variety of alloys up to a maximum intake of 4.4 Li per Sn atom to form $\text{Li}_{4.4}\text{Sn}$.

Recently, interest in metal oxides such as Al_2O_3 , MgO and TiO_2 has been largely stimulated by the realization that they can improve the cycling stability of the Li-ion battery electrodes. Titanium dioxide exists in different polymorphic forms, such as rutile, anatase and brookite. Of the various polymorphs of TiO_2 , both the rutile and brookite can accommodate only small amounts of lithium, while the anatase phase has different ratios of lithium insertion. A metal oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, is a promising candidate as a negative electrode in solid, liquid and gel Li-ion batteries. Electrode does not experience the passivation of carbon materials and their inevitable electrolyte reaction. In view of the above reasons we are evaluating the commercially obtained metal oxides electrochemically to obtain the preliminary data and improve our anode material. Our goal is to make a better metal oxide anode material, which addresses all the problems encountered in using graphite anode material. In the preliminary results obtained for the SnO_2 anode we obtained a first discharge capacity of 1400mAhg^{-1} which is much higher than the theoretical capacity of SnO_2 . The cyclic voltammogram of SnO_2 with lithium as the counter electrode scanned at 0.2 mV/s shows the peak around 0.9V , which is ascribed to the irreversible conversion of SnO_2 to Sn and Li_2O . We noticed a disappearance of the first peak in the subsequent scans at 0.3 and 0.4 mV/s (not shown in this report) is because of the irreversibility of formation of lithia, which corresponds to the large irreversible capacity. Well-defined peaks corresponding to the several alloy phases suggests that the necessary rearrangements of the constituent atoms to nucleate the various phases of different crystal structures are slow or are kinetically hindered. The processes being diffusion-controlled manifest as a single-phase transformation. Moreover, the shoulder around 1.25V , suggesting that the reduction of Sn(IV) to Sn(0) occurs via Sn(II) , is in agreement with the earlier observations.

In Fig 4a for commercial (micro) TiO_2 (Aldrich) the reduction of Ti^{4+} to Ti^{3+} takes place at 1.65V and the corresponding deinsertion (oxidation) takes place at 2.14V . The peak separation is determined by the over potential required for the transformation of TiO_2 to Li_xTiO_2 . In Fig 4b, as can be seen, there is a plateau in the 1.75V region. The first discharge capacity was 230mAhg^{-1} . In the tenth cycle the discharge capacity i.e. very low because of the irreversible capacity and

poor cycleability. This we are trying to improve by adding metal nanoparticles to improve the conductivity of the titania electrode. Although the theoretical capacity of anatase TiO_2 is 330-mAh g^{-1} , the practical achievable capacity is only half of the available capacity. This is mainly because of the fact that, presence of Li greater than $x = 0.5$ in Li_xTiO_2 leads to strong Li–Li interaction in the lattice. The main redox reaction responsible for the electrochemical activity is the conversion $\text{Ti}^{4+}/\text{Ti}^{3+}$ during the discharge process and vice versa during the charge process.

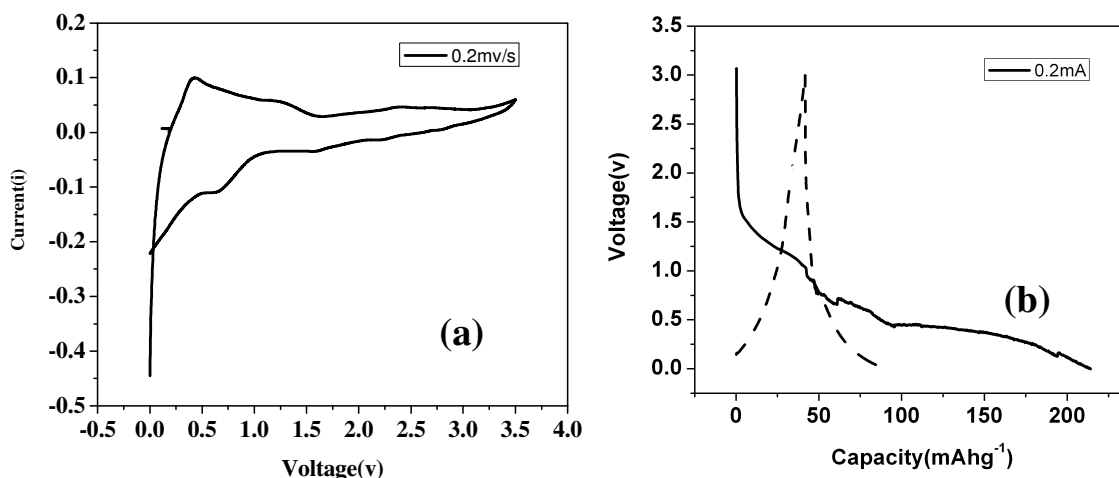


Fig.4 (a) Cyclic voltammogram of TiO_2 /Li coin cell: (b) Room temperature charge-discharge characteristics of the first ((solid line) 1C, 1D, 10C, 10D(dashed line) TiO_2 /Li coin cell at 0.2 mA/cm^2 between 0 V and 3 V.

1.4 Fabrication of prototype batteries

The construction of a prototype battery was done using carbon nanotubes as anode and $\text{LiCr}_{0.05}\text{Mn}_{1.75}\text{O}_4$, $\text{Li}_{1.2}\text{Mn}_{1.95}\text{Al}_{0.05}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.46}\text{Rh}_{0.04}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as cathode material and characterization by electrochemical methods. We have fabricated a prototype battery using $\text{LiMn}_{1.5}\text{Ni}_{0.46}\text{Rh}_{0.04}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as cathode material and SWCNTs as anode material. The cyclic voltammetry reveals lithium intercalation/deintercalation through SWCNTs and peaks corresponding to Mn and Ni redox couple. All the above prototype batteries are under experimental evaluation for charge discharge properties. Encouraged by the promising result, we are planning to extend this work, by combining, best performing cathode, electrolyte and anode materials.

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Human Resource Developments: (May 2004 – April 2008)

Doctoral thesis completed: 2 (S. Nieto-Ramos, Ricardo Melgarejo)

MS thesis completed: 2 (S.R. Das, O. Oviedo)

Post-doctoral fellows: 3 (R. Singhal, B. Natesan, M.K. Singh, R. Thomas)

Doctoral work in Progress: 5 (N.K. Karan, J. Saavedra, H. Yilmaz, A. Kumar, S. Sivaparakash)

Undergraduate students: 3 (Juan Burgos, Itzier Menses, C. Villanueva)

Educational activities (together with the NASA and AMP Projects)

Three doctoral students were awarded DoE fellowships from the project each year. These students were selected from a pool of ~ 96 graduate students working for their Ph.D. degrees in different fields and who had applied for the doctoral fellowships with the Resource Center for Science and Engineering.

List of DOE-EPSCoR Project Publications: (May 2004 to April 2008)

1. Improvement of the cycleability of nano-crystalline lithium manganate cathodes by cation co-doping, *Journal of Power Sources* **136** 88 (2004).
2. Experimental and theoretical studies of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{M}_{1/3}\text{O}_2$ [M =Mo and Rh] for cathode material, S.P. Singh, M.S. Tomar, Y. Ishikawa, *Microelectronics Journal*, **36** 491 (2005).
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7. Ion Relaxation Dynamics and Nearly Constant Loss Behavior in Polymer Electrolyte, B. Natesan, N. Karan, and R.S. Katiyar, *Physics Review*, **E74**, 042801 (2006)
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